ABSTRACT

The emission spectrum of Eu tetrakis(dibenzoylmethide)piperidinium in crystalline powder at 77°K was analyzed in detail employing first-order perturbation theory. The complete equivalence between a crystalline field and a molecular (ligand) field in chelates with respect to the Stark splitting of the intra-4f levels was demonstrated. The existence of two stereoisomers was established and found consistent with a dodecahedral and an antiprismatic configuration. The most likely assignment for the fluorescence lines was found for each of the two isomers. The ligand field parameters for the equivalent point charge models of the two stereoisomers were determined. The conclusions about the shape of the two molecular species drawn from these parameters are consistent with the configuration of dodecahedron and distorted antiprism respectively. A satisfactory agreement was found between experiment and theory.

ANALYSIS OF FLUORESCENCE SPECTRA OF RARE EARTH CHELATES
I. INTERNAL STARK SPLITTING IN EUROPIUM DIBENZOYLMETHIDE

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Introduction

Narrow line fluorescence is observed in certain Eu complexes when excited with light absorbed by the organic ligand as a result of intramolecular energy transfer. The absence of broad line fluorescence characteristic of rare earth ions incorporated in nonhomogeneous surroundings (e.g. glasses) indicates the presence of the same environment for all Eu ions similar to that present in doped single crystals.

The purpose of the present paper is to investigate whether the splitting of the lines of Eu chelates in the fluorescent spectrum can be explained in terms of a perturbation produced by the electrostatic effect of the ligand field on the Eu^{3+} ion. This can be done assuming that the ligand field splitting is small in comparison with the spin-orbit coupling, so that the unsplit energy levels in $^7F_1$, E_o, are treated as variable parameters to be determined, and the splitting of these levels is treated as being produced by the ligand field. Further, we propose to determine the ligand field parameters from the experimental data and to assign the experimental values of the energy levels to the various possible stereoisomers.

First, we prove the complete equivalence between a ligand field and a crystal field of corresponding symmetry with respect to their electrostatic effects on the fluorescence spectrum of the rare earth ion. This result is used to analyze the emission spectrum of Eu dibenzoylmethide employing first-order perturbation theory.

Experimental

Preparation of Chelate - Eu tetrakis(dibenzoylmethide)piperidinium (EuD_4P) was prepared by adding 8 mmoles of piperidine in 10ml. absolute ethanol to a hot mixture of 8 mmoles of dibenzoylmethane and 2 mmoles of anhydrous $EuCl_3$ in 70ml. absolute EtOH. The clear solution was allowed to cool slowly overnight to room temperature. The well defined light yellow needles were filtered, washed with small portions of cold ethanol, air dried, and recrystallized twice from absolute EtOH. The chelate melted sharply at 186-186.5°C (uncorrected).

Fluorescence Spectrum - The crystals were sealed with nonfluorescence tape between two quartz slides and lowered in a quartz dewar containing liquid nitrogen. Light from a 1000 watt, water cooled high pressure AH-6 mercury arc was filtered through a $NiSO_4$ water solution and a Corning CS7-54 filter and directed into a metal box constructed to minimize stray light. The clear bottom part of the dewar was positioned in the box such that the exciting light was focused on the sample. The fluorescence emission was directed through a Corning CS3-70 filter into a Cary Model 14 spectrophotometer and detected by a R136 red-sensitive photomultiplier. The entrance

slit to the Cary was adjusted manually for different spectral regions to control the intensity of the light entering the monochromator. Dry air was caused to circulate inside the box to prevent possible fr[illegible]ing on the dewar. The recorded fluorescence spectrum is shown in Figure 1.

Equivalence of Ligand and Crystal Fields - Let r, θ, φ be the coordinates of a point in the electric field produced by a charge-distribution of density $\rho(\underset{\sim}{r}')$ originating in the ligand. We can consider $\rho(\underset{\sim}{r}')$ as being the time and space average over the entire ketoenolate structure as represented by both σ bonds frame and delocalized π-electrons. The potential is given by:

$$V(r,\theta,\varphi) = V(\underset{\sim}{r}) = \int \frac{1}{|\underset{\sim}{r}-\underset{\sim}{r}'|}\, \rho(\underset{\sim}{r}')\, d\tau' \qquad (1)$$

integrated over the source points with coordinates $\underset{\sim}{r}'$.

As is well known

$$\frac{1}{|\underset{\sim}{r}-\underset{\sim}{r}'|} = 4\pi \sum_{l,m} \frac{r^l}{(2l+1)\, r'^{l+1}}\, Y_l^m(\theta,\varphi)\, Y_l^{m*}(\theta',\varphi') \qquad (2)$$

Consequently, the potential (1) can be written

$$V(r,\theta,\varphi) = 4\pi \sum_{l,m} \frac{r^l\, Y_l^m(\theta,\varphi)}{2l+1} \int \frac{Y_l^{m*}(\theta',\varphi')\, \rho(\underset{\sim}{r}')\, d\tau}{r'^{l+1}} \qquad (3)$$

For a crystal field with point charges q_i at the points $\underset{\sim}{r}_i$, the charge density $\rho(\underset{\sim}{r}')$ would be given by

$$\rho(\underset{\sim}{r}') = \sum_i q_i\, \delta(\underset{\sim}{r}-\underset{\sim}{r}_i) \qquad (4)$$

and the integrals in (4) would reduce to

$$A_l^m = 4\pi \sum_i \int \frac{q_i\, Y_l^{m*}(\theta',\varphi')\, \delta(\underset{\sim}{r}-\underset{\sim}{r}_i)\, d\tau}{(2l+1)\; r_i'^{l+1}} \qquad (5)$$

or

$$A_\ell^m = 4\pi \sum_i \frac{q_i}{(2\ell+1)\, r_i'^{\ell+1}} Y_\ell^{m*}(\theta_i, \varphi_i) \tag{6}$$

The equivalent integrals for the ligand field are

$$\alpha_\ell^m = 4\pi \int \frac{Y_\ell^{m*}(\theta', \varphi')\, \rho(r')\, d\tau}{(2\ell+1)\, r'^{\ell+1}} \tag{7}$$

Thus the potential produced by the ligand field is given by

$$V(r, \theta, \varphi) = \sum_{\ell, m} \alpha_\ell^m r^\ell Y_\ell^m(\theta, \varphi) \tag{8}$$

whereas the expression for the potential for a crystal field is

$$V(r, \theta, \varphi) = \sum_{\ell, m} A_\ell^m r^\ell Y_\ell^m(\theta, \varphi)$$

Consequently a ligand field has the same potential as a crystal field, in spite of the delocalized electron density associated with the anion-ligand configuration, and will produce the same internal Stark splitting of the energy levels as the equivalent crystal field, provided

$$\alpha_\ell^m = A_\ell^m$$

It may well be that to produce the actual field, one needs an infinite number of point charges to get all the parameters α_ℓ^m equal to A_ℓ^m. This, however, is not the point. What one needs in the calculations of internal Stark splitting is not the total field but only a small number of parameters α_ℓ^m and these can always be found from a small number of point charges.

Therefore, one can always find a hypothetical field produced by point charges which will have the same effects on the spectrum as the molecular (ligand) field. We note that no dipoles or higher moments are needed. One might think that a charge distribution spread out over a number of atoms

as found in the ketoenolate anion would tend to give rise to broadened fluorescence lines whereas point charges as in the crystal field model would give sharp lines.. This however is not the case. In first-order perturbation theory the energy levels are given by the roots of the secular determinant in terms of the parameters α_ℓ^m and Λ_ℓ^m respectively, and both of these will give discrete solutions to the secular equation.

Having established the equivalence between the ligand field and a crystal field, we can employ the operator equivalent methods developed for crystal field problems by Judd[1] and Stevens[2].

Analysis of the Eu Tetrakis-Dibenzoylmethide Piperidinium Fluorescence Spectrum - This particular chelate has been selected because of the symmetry of the ketoenolate groups surrounding the Eu^{3+} ion, which in turn will lead to a small number of ligand field parameters α_ℓ^m. This fact is essential in the calculation of the α_ℓ^m's from experimental data.

For such compounds, the ligand field parameters can be found employing only transitions from the excited $^5D_0$ state to $^7F_0$, $^7F_1$, and $^7F_2$ levels in the ground multiplet of Eu ion. In less symmetrical systems such as chelates from differently substituted β-diketones, transitions terminating at the $^7F_3$ level may prove to be necessary. However, in this case, the solutions of the secular determinant are so complex that very probably they cannot be correlated to experimental data.

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1. (a) B. R. Judd, Mol. Phys., 2, 407 (1959); (b) ibid., Proc. Roy. Soc., A228, 120 (1955)
2. K. W. H. Stevens, Proc. Phys. Soc., 65, 209 (1952)

The fluorescence spectrum of EuD_4P in microcrystalline powder at 77°K is shown in Figure 1. All the emission lines observed in the range 5700 to 6400Å correspond to transitions from ^5D_o to ^7F_o, and $^7F_2$ levels as pointed out by Freeman and Crosby[3].

To be more specific, the unsplit line at 5800Å is the $^5D_o \rightarrow {}^7F_o$ transition; the 5 lines at 5905, 5914, 5924, 5955, and 5986Å are $^5D_o \rightarrow {}^7F_1$ transitions and the 9 lines at 6043, 6119, 6125, 6132, 6137, 6255, 6307, 6333, and 6373Å are $^5D_o \rightarrow {}^7F_2$.

The maximum number of sublevels into which a ^7F_J level splits is equal to its degeneracy $2J + 1$, or 1, 3, and 5 lines respectively for ^7F_o, $^7F_1$, and $^7F_2$ levels. The presence of more lines than expected clearly indicates the existence of two stereoisomers. The orbitals available for bonding in the Eu ion are the empty 5d, 6s, and 6p orbitals. The fact that the partially occupied 4f orbitals are not involved in bonding is indicated by the discrete structure of both absorption and emission spectra of the chelated ion and their similarity with those of inorganic ionic salts. There are only two possibilities for the lanthanide ion to accommodate eight coordinating oxygen atoms: a dodecahedral arrangement for the use of d^4sp^3 hybrid orbitals (Model A), and an antiprismatic configuration for d^4sp^3 and d^5p^3 (Model B).[4]

Perturbation Calculation - Assume that the Hamiltonian can be broken up into two parts $H = H_o + H'$ where H_o is the Hamiltonian of the 4f electrons of the free ion and H' is eV with V the electrostatic potential produced by the ligand and given by equation (8). H' is assumed small in comparison with H_o

3. J. J. Freeman and G. A. Crosby, J. Phys. Chem., 67, 2717 (1963)
4. (a) A. F. Wells, "Structural Inorganic Chemistry" Oxford University Press, 1962; (b) G. E. Kimball, J. Chem. Phys., 8, 188 (1940)

or $\sum \zeta(r_i)\, \vec{l}_i \cdot \vec{s}_i \gg H'$. H_o is invariant with respect to rotation around the origin which means that the total angular momentum J of the 4f electrons in the unperturbed ion is a good quantum number and energies of the degenerate levels ^7F_J are the eigenvalues of H_o. We need to calculate the splitting of the ^7F_o, $^7F_1$ and $^7F_2$ levels caused by eV.

The first part of the Stevens and Judd method consists of expressing the $r^l Y_l^m$ terms as polynominals in powers of r, x, y, and z. That part of (8) which we will need then becomes:

$$V(r,\theta,\varphi) = \beta_2^0 (3z^2 - r^2) + \beta_2^2 (x^2 - y^2) + \beta_4^0 (35z^4 - 30r^2z^2 + 3r^4) + \beta_4^2 (7z^2 - r^2)(x^2 - y^2) + \beta_4^4 (x^4 - 6x^2y^2 + y^4) \quad (10)$$

with

$$\beta_2^0 = \frac{1}{4}\left(\frac{5}{\pi}\right)^{\frac{1}{2}} \alpha_2^0 \quad , \quad \beta_2^2 = \frac{1}{4}\left(\frac{15}{\pi}\right)^{\frac{1}{2}} \alpha_2^2$$
$$\beta_4^0 = \frac{3}{16}\left(\frac{1}{\pi}\right)^{\frac{1}{2}} \alpha_4^0 \quad , \quad \beta_4^2 = \frac{3}{8}\left(\frac{5}{\pi}\right)^{\frac{1}{2}} \alpha_4^2 \quad (11)$$
$$\beta_4^4 = \frac{3}{16}\left(\frac{35}{\pi}\right)^{\frac{1}{2}} \alpha_4^4$$

Since in the case of molecules, the structure of the equivalent point charge configuration may not fall into any of the crystal symmetries, we do not use group theoretical arguments to show that only those parameters listed above are needed but show this directly. First, we consider the dodecahedral configuration and assume that this molecule can, in this case, be represented by eight equal charges for which $\varphi_1 = \varphi_2 = 0$, $\varphi_3 = \varphi_4 = \frac{\pi}{2}$, $\varphi_5 = \varphi_6 = \pi$ $\varphi_7 = \varphi_8 = \frac{3\pi}{2}$, and $\theta_1 = \theta_5 + \theta_3 = \theta_7$, $\theta_1 + \theta_4 = \theta_3 + \theta_6 = \theta_5 + \theta_8 = \theta_7 + \theta = \pi$ There is thus twofold rotational symmetry around the z-axis. Consequently $e^{im\varphi} = e^{im(\varphi+\pi)} = 1$ or $m = 0, 2, 4 \cdots$ All terms for $l > 6$ have zero

matrix elements. The matrix elements leave the form $\int \psi_1^* V \psi_2 \, d\tau$, where ψ_1 and ψ_2 are f-electron wave functions ($l_1 = l_2 = 3$). When $\psi_1^* \psi_2$ is expanded in terms of spherical harmonics, the highest l in this expansion is C = 6. For terms in V with $l > 6$ the matrix element vanishes because of the orthogonality of the spherical harmonics. From the properties of the 3 -J coefficients in this expansion one finds that l must be even. For the states $^7F_0$ - $^7F_2$ the coefficient of proportionality between the point charge field and the equivalent angular momentum operators is zero for l = 6. Omitting the constant β_0^0 we are left with the following coefficients contributing to the $^7F_2$ splittings $\beta_2^0, \beta_2^2, \beta_4^0, \beta_4^2, \beta_4^4$. For the dodecahedral configuration the terms Y_2^2 and Y_4^2 add up to zero upon taking into account the relation.

$$P_l^m(-x) = (-1)^{m+l} P_l^m(x)$$

Thus only the parameters $\beta_2^0, \beta_4^0, \beta_4^4$ contribute to the splitting of the $^7F_2$ level for the dodecahedral configuration.

For the antiprismatic configuration we assume the existence of an equivalent point-charge model with eight equal charges with $\theta_1 = \theta_2 = \theta_3 = \theta_4$, $\theta_5 = \theta_6 = \theta_7 = \theta_8$, $\theta_1 + \theta_5 = \pi$. $\varphi_1 = -\varphi_6$, $\varphi_2 = -\varphi_5$, $\varphi_3 = -\varphi_8$, $\varphi_4 = -\varphi_7$, $\varphi_3 - \varphi_1 = \pi$, $\varphi_4 - \varphi_2 = \pi$.

Repeating the arguments above one finds that the following coefficients contribute to the splitting of the $^7F_2$ level: $\beta_2^0, \beta_2^2, \beta_4^0, \beta_4^2, \beta_4^4$.

Substituting the angular momentum operators J, J_z, J_+, and J_- into (11) V(r, θ, φ) becomes

$$V(r,\theta,\varphi) = \alpha_J \langle r^2\rangle \beta_2^0 \left[3J_z^2 - J(J+1)\right] + \alpha_J \langle r^2\rangle \beta_2^2 \tfrac{1}{2}\left[J_+^2 + J_-^2\right]$$
$$+ \beta_J \langle r^4\rangle \beta_4^0 \left[35J_z^4 - 30J(J+1) + 25J_z^2 - 6J(J+1) + 3J^2(J+1)^2\right]$$
$$+ \beta_J \langle r^4\rangle \beta_4^2 \tfrac{1}{4}\left\{\left[7J_z^2 - J(J+1) - 5\right]\left(J_+^2 + J_-^2\right) + \left(J_+^2 + J_-^2\right)\left(7J_z^2 - J(J+1) - 5\right)\right\} + \beta_J \langle r^4\rangle \beta_4^4 \cdot \tfrac{1}{2}\left[J_+^4 + J_-^4\right] \qquad (12)$$

where[5] $\alpha_0 = \beta_0 = \beta_1 = 0$, $\alpha_1 = -\frac{1}{5}$, $\beta_2 = -\frac{2}{105}$, $\alpha_2 = -\frac{11}{315}$.

The $^7F_0$ level will remain unsplit which agrees with the experiment. The secular determinant for $^7F_1$ with matrix elements $\langle M'J'|eV|JM\rangle$ is

$$\begin{vmatrix} \langle -11|eV|1-1\rangle - E & \langle -11|eV|10\rangle & \langle -11|eV|11\rangle \\ \langle 01|eV|1-1\rangle & \langle 01|eV|10\rangle - E & \langle 01|eV|11\rangle \\ \langle 11|eV|1-1\rangle & \langle 11|eV|10\rangle & \langle 11|eV|11\rangle - E \end{vmatrix} = 0$$

Using (12) the secular determinant reduces for the dodecahedron (S_4 symmetry) to

$$\begin{vmatrix} \alpha_1\langle r^2\rangle\beta_2^0 - E & 0 & 0 \\ 0 & -2\alpha_1\langle r^2\rangle\beta_2^0 - E & 0 \\ 0 & 0 & \alpha_1\langle r^2\rangle\beta_2^0 - E \end{vmatrix} = 0$$

with solutions $E_1 = E_2 = \alpha_1\langle r^2\rangle\beta_2^0$ and $E_3 = -2\alpha_1\langle r^2\rangle\beta_2^0$. For the antiprism B ($D_4$ symmetry) the secular determinant is

$$\begin{vmatrix} \alpha_1\langle r^2\rangle\beta_2^{0\prime} - E & 0 & \alpha_1\langle r^2\rangle\beta_2^{2\prime} \\ 0 & -2\alpha_1\langle r^2\rangle\beta_2^{0\prime} - E & 0 \\ \alpha_1\langle r^2\rangle\beta_2^{2\prime} & 0 & \alpha_1\langle r^2\rangle\beta_2^{0\prime} - E \end{vmatrix} = 0$$

5. B. R. Judd, Op. Cit. p. 408.

With solutions

$$E_4 = -2\alpha_1 \langle r^2 \rangle \beta_2^{0\prime}$$
$$E_5 = \alpha_1 \langle r^2 \rangle \beta_2^{0\prime} + \alpha_1 \langle r^2 \rangle \beta_2^{2\prime}$$
$$E_6 = \alpha_1 \langle r^2 \rangle \beta_2^{0\prime} - \alpha_1 \langle r^2 \rangle \beta_2^{2\prime} \qquad (13)$$

We should thus have five lines in the region corresponding to the $^5D_0 \rightarrow {}^7F_1$ transition which agrees with experiment. The secular determinant for the dodecahedron gives the following energy levels for the $^7F_2$:

$$E_1 = E_2 = E_0 - 3\alpha_2 \langle r^2 \rangle \beta_2^0 - 48\beta_2 \langle r^4 \rangle \beta_4^0$$
$$E_3 = E_0 - 6\alpha_2 \langle r^2 \rangle \beta_2^0 + 72\beta_2 \langle r^4 \rangle \beta_4^0$$
$$E_4 = E_0 + 6\alpha_2 \langle r^2 \rangle \beta_2^0 + 12\beta_2 \langle r^4 \rangle \beta_4^0 + 12\beta_2 \langle r^4 \rangle \beta_4^4$$
$$E_5 = E_0 + 6\alpha_2 \langle r^2 \rangle \beta_2^0 + 12\beta_2 \langle r^4 \rangle \beta_4^0 - 12\beta_2 \langle r^4 \rangle \beta_4^4 \qquad (14)$$

The energy levels given by solving the secular determinant for the antiprism are:

$$E_6 = E_0 + 6\alpha_2 \langle r^2 \rangle \beta_2^{0\prime} + 12\beta_2 \langle r^4 \rangle \beta_4^{0\prime} - 12\beta_2 \langle r^4 \rangle \beta_4^{4\prime}$$
$$E_7 = E_0 - 3\alpha_2 \langle r^2 \rangle \beta_2^{0\prime} - 48\beta_2 \langle r^4 \rangle \beta_4^{0\prime} - 3\alpha_2 \langle \beta_2^{2\prime} \langle r^2 \rangle + 12\beta_2 \langle r^4 \rangle \beta_4^{2\prime}$$
$$E_8 = E_0 - 3\alpha_2 \langle r^2 \rangle \beta_2^{0\prime} - 48\beta_2 \langle r^4 \rangle \beta_4^{0\prime} + 3\alpha_2 \langle r^2 \rangle \beta_2^{2\prime} - 12\beta_2 \langle r^4 \rangle \beta_4^{2\prime}$$
$$E_9 = E_0 + \frac{84\beta_2 \langle r^4 \rangle \beta_4^{0\prime} + 12\beta_2 \langle r^4 \rangle \beta_4^{4\prime} + X}{2} \qquad (15)$$
$$E_{10} = E_0 + \frac{84\beta_2 \langle r^4 \rangle \beta_4^{0\prime} + 12\beta_2 \langle r^4 \rangle \beta_4^{4\prime} - X}{2}$$

with

$$X = \Big[\left(84\beta_2 \langle r^4 \rangle \beta_4^{0\prime} + 12\beta_2 \langle r^4 \rangle \beta_4^4\right)^2 - 24\left(-\alpha_2 \langle r^2 \rangle \beta_2^{0\prime} + \beta_2 \langle r^4 \rangle \beta_4^{0\prime}\right)$$
$$\left(6\alpha_2 \langle r^2 \rangle \beta_2^{0\prime} + 12\beta_2 \langle r^4 \rangle \beta_4^{0\prime} + 12\beta_2 \langle r^4 \rangle \beta_4^{4\prime}\right) + 48\left(\alpha_2 \langle r^2 \rangle \beta_2^{2\prime} + 3\beta_2 \langle r^4 \rangle \beta_4^{2\prime}\right)^2 \Big]^{\frac{1}{2}} \qquad (16)$$

Comparison with Experiment

The $^5D_0 \rightarrow {}^7F_0$ transition is easily identified with the unsplit line at 17241 cm^{-1}. The energy of the $^5D_0$ level is observed to be the same for both

the "dodecahedron" and the "archimidean antiprism", resulting in one superimposed fluorescence line.

Careful analysis of the fluorescence spectra of several tetrakis β-ketoenates having the same basic structure as EuD_4P showed the presence of three strong lines in the $^5D_o \rightarrow {}^7F_1$ region. This common feature is found also in the spectra of tetrakis chelates in which one single species is responsible for all the emission lines such as the benzoylacetonate. Therefore, the lines at 16935, 16880, and 16793 cm^{-1} were assigned to the antiprism stereoisomer which is expected to have three $^7F_1$ Stark components, and the weaker lines at 16909 and 16706 cm^{-1} were attributed to the dodecahedron. When the $^7F_1$ components corresponding to the three stronger lines were substituted for E_3, E_4, and E_5 in equation (13), two assignments were found to be possible. This yields, as a result, two sets of values for the $\beta_2^{0\prime}$ and $\beta_2^{2\prime}$ parameters. The selection between the two possible assignments was made only after analysis of the $^5D_o \rightarrow {}^7F_2$ transitions.

Common features observed in the $^5D_o \rightarrow {}^7F_2$ range for different tetrakis β-ketoenolates led us to the assignment of the following levels to the antiprism stereoisomer: 16342, 16307, 16215, 15987, and 15855 cm^{-1}. Other assignments were considered, however, and were found to be impossible. The ratios of the A parameters were used to verify this and other apparently possible assignments and to prove the correctness of the selected assignment for the predominant stereoisomer, the antiprism. The angular restrictions imposed on the model by this assignment allowed the proper selection of only one of the two sets of values for the $\beta_2^{0\prime}$ and $\beta_2^{2\prime}$ parameters from the $^5D_o \rightarrow {}^7F_1$ lines. The remaining four lines at 16548, 16326, 15790, and 15691 cm^{-1} in the $^5D_o \rightarrow {}^7F_2$

region were attributed to the "dodecahedral" stereoisomer. Employing the equations (14), a unique assignment is found for the four $^7F_2$ Stark components in agreement with the dodecahedral model.

The results are:

For the dodecahedron:

915 = $E_1 = E_2$

1550 = E_3 Eo = 1105 cm^{-1}

1451 = E_4

623 = E_5

For the antiprism:

899 = E_6

1254 = E_7 Eo = 1100 cm^{-1}

1026 = E_8

1386 = E_9

934 = E_{10}

The ligand field parameters are:

For the dodecahedron:

$B_2^0 = +340$, $B_4^0 = -528$, $B_4^4 = -2985$

For the antiprism:

$B_2^0 = +190$, $B_2^2 = -135$, $B_4^0 = +79$, $B_4^2 = +1668$, $B_4^4 = -189$

The ratio between parameters having the same ℓ are functions of the angles only.

Conclusion

We have demonstrated the complete equivalence between a crystalline field and the molecular (ligand) field in Eu chelates with respect to the Stark splitting of the intra-4f energy levels.

The existence of two stereoisomers in crystalline EuD_4P was established and their fluorescence spectra were found to be consistent with a dodecahedral and antiprismatic configuration for the two isomers.

The most likely assignment for the fluorescence lines in the ^5D_o to ^7F_o, $^7F_1$ and $^7F_2$ regions was found for each individual stereoisomer.

The ligand field parameters for the equivalent point charge models associated with each of the two stereoisomers were determined. The conclusions about the shape of the two molecular species drawn from these parameters are consistent with the dodecahedron and the antiprism. The agreement between experiment and theory is satisfactory.

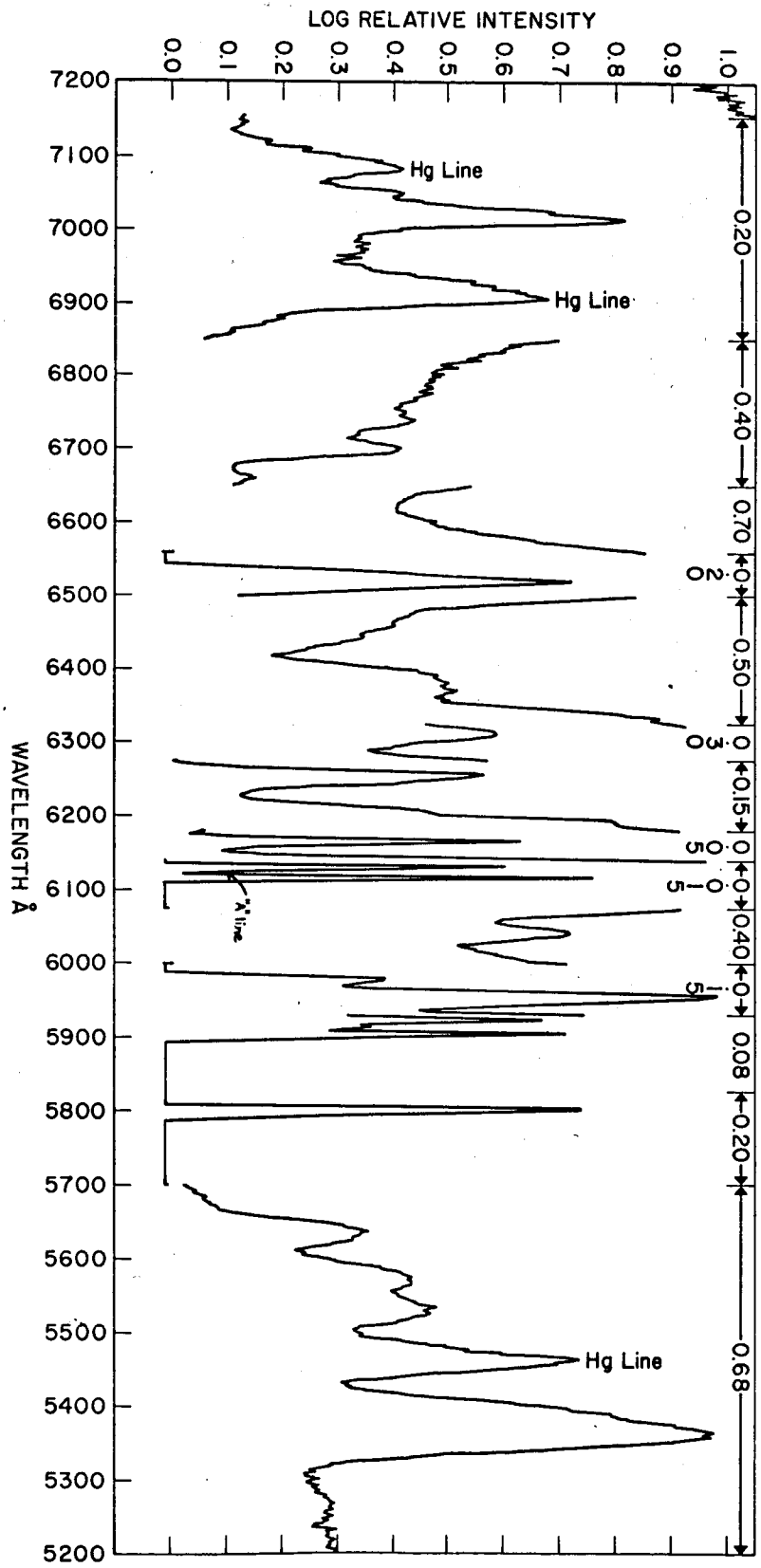
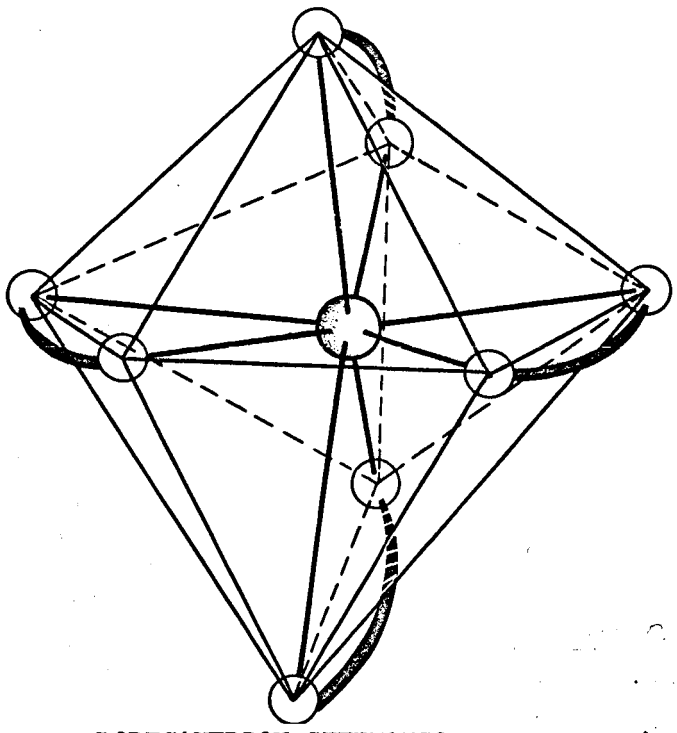
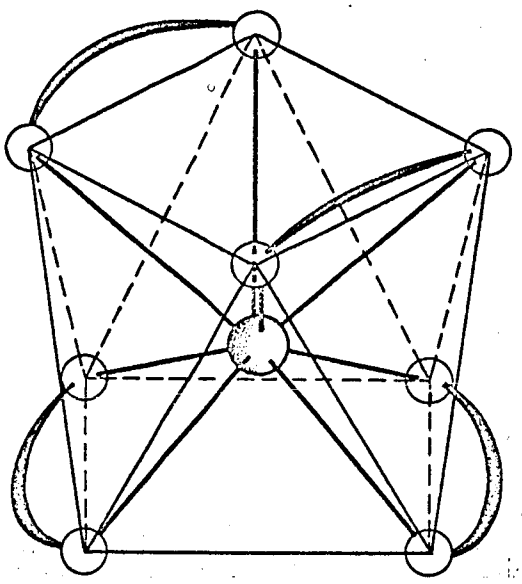


Figure 1. Fluorescence spectrum of Eu tetrakis(dibenzoylmethide)piperidinium in microcrystalline powder at 77°K. The slit-width in mm. is given at the top.



DODECAHEDRON STEREOISOMER



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